16

CONSTITUTION OF WATER IN SOLUTIONS OF STRONG ELECTROLYTES.*—II.

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ABSTRACT. In continuation of the earlier work of the author, the following substances have been investigated with a view to determine their influence on the constitution of water in their aqueous solutions; $LiNO_3$, LiCl, $CaCl_2$, $CaBr_2$, $NaNO_3$, $NaClO_3$, $NaClO_4$ and $HClO_4$. The following are some of the main results observed :

(*i*) The Raman water-band in solutions is invariably sharper than in the pure solvent and is shifted, in general, to higher frequency.

(*ii*) At the same concentration of the salt solutions, there is a progressive shift in the band to higher frequency from $CaCl_2$ to $CaBr_2$ and $LiNO_3$ to $NaNO_3$, that in the case of the last named being the greatest.

(*iii*) The close similarity between the bands at the same water content observed with the acid solutions before is not so obvious with the salts.

(*iv*) The water-band in $HClO_4$ is particularly sharp and shifted most to higher frequency, while among the sodium salts studied, the band for $NaClO_4$ is the least sharp.

(*v*) The chlorides behave differently from the bromides.

(*vi*) The position of the intensity maximum of the water-band in solutions is characteristic of the anion and independent of the nature of the cation.

The above results are discussed in detail on the basis of a change in water equilibrium and of ionic hydration and explanations arrived at. In particular, it has been shown that change in water equilibrium is primarily brought about by the anion, while changes in the structure of the band due to hydration are mainly due to the cation.

1. INTRODUCTION.

In a previous communication,[1] the author has published the results of a detailed study by means of the Raman effect of the influence of a number of strong electrolytes—both acids and salts—on the constitution of water, when they are dissolved in it. Therein, it has been found that the influence of the dissolved electrolyte is to invariably sharpen the Raman band for water and shift it in most cases towards higher frequency. Further, the differences noticed in the structure of the band in the solutions of different substances when studied at the same concentration tended to disappear when the water content in them was equalized. The results obtained were discussed at length on the basis of the two possible

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causes of the change in the distribution of intensity along the Raman water-band, namely, a change in the water equilibrium between the proportions of the single $(H_2O)_1$, double $(H_2O)_2$ and triple $(H_2O)_3$ molecules assumed to exist in water, and ionic hydration of the molecules of the dissolved substance.

In the above study it has been noticed that the behaviour of substances containing the chloride ion—hydrochloric acid and lithium chloride were the only substances that could be then examined—was peculiar from that of the others, and it was, therefore, felt desirable to see whether chlorides alone or halides as a class behave in this manner by studying some more substances of this kind. Further, in order to generalize the conclusions arrived at before regarding the behaviour of strong electrolytes in their aqueous solutions, some more substances of this category have now been investigated.

Magat,[2] in a recent paper, studied the influence of certain strong electrolytes, namely some chlorides and nitrates of divalent and tetravalent elements, on the structure of the Raman water-band and found that the 3200 cm^{-1} component is, in general, weakened as compared with the second component at 3400 cm^{-1}, that its displacement primarily depends on the nature of the anion, the cation exercising little influence, and that it was small for chlorides and large for nitrates. The author is interested more with a satisfactory interpretation of the results obtained than with a mere enumeration of them, and has, in addition to chlorides and nitrates, studied other typical electrolytes under higher concentrations, the results obtained with which are described in the succeeding pages of this communication.

2. EXPERIMENTAL.

The experimental arrangement employed in the present investigations was, in most cases, that described in an earlier paper.[3] Sometimes, a number of filtering solutions had to be tried before a spectrum could be obtained without any continuous background, which was often so great in the unfiltered incident radiation as to make it almost impossible to obtain any reliable results. In this, as also in the previous study on this subject, the water-band excited by the 3650-63Å group of mercury lines was employed for reasons explained in Part I of this investigation. Further, the study was confined to those substances which dissolve to high concentrations—8N and above—as it was only then that unambiguous results as to the influence of the dissolved substance on the constitution of the solvent could be obtained. And, as very few substances dissolve to such high concentrations, the choice has to be limited only to those which are very highly soluble. Of these again, those substances which photochemically dissociate on exposure to the ultra-violet radiation from the mercury arc, *e.g.*, potassium iodide, and those which are naturally deeply coloured, *e.g.*, hydrobromic acid, had to be left out for obvious reasons.

3. RESULTS.

Figure 1 gives the intensity curves of the Raman water-band excited by the 3650λ group in solutions of the two salts, lithium chloride and nitrate, when studied at the same concentration, *viz.*, 8N. The curve for the band in pure water is also given for purposes of mutual comparison. The distribution of intensity along the water-band in the two solutions and pure water is given in table I below.

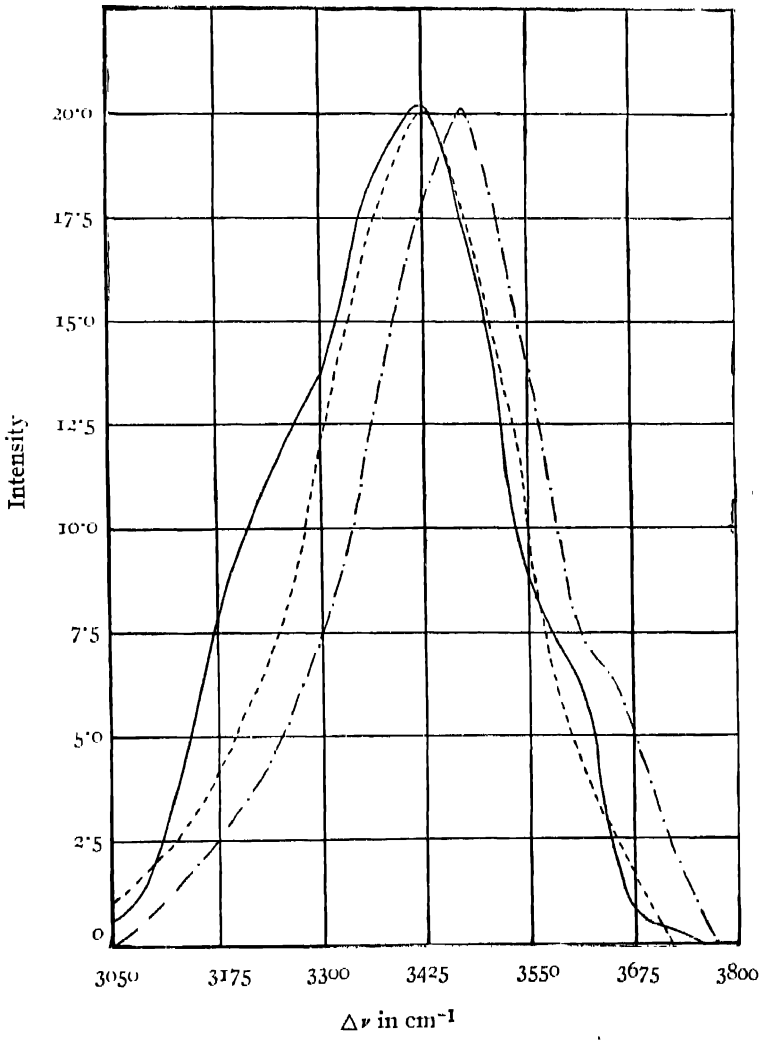

FIGURE 1

Intensity curves for the Raman-water-band in solutions of $LiNO_3$ and LiCl at the same concentration (8N) and in pure water.

H_2O ——— ; $LiNO_3$, 8N - · - · - · - ; LiCl, 8N - - - - - - -

TABLE I.

Intensity distribution along the water-band in

1. Pure water.		2. $LiNO_3$, 8N.		3. LiCl, 8N.		4. LiCl, 4·2N.	
$\delta\nu$ in cm^{-1}.	Intensity.	$\delta\nu$ in cm^{-1}.	Intensity.	$\delta\nu$ in cm^{-1}.	Intensity.	$\delta\nu$ in cm^{-1}.	Intensity.
3013	0·20	3122	1·27	3051	1·03	3019	0·50
3063	0·72	3194	2·99	3110	2·12	3093	1·69
3157	6·13	3278	6·29	3175	4·12	3171	3·32
3233	9·89	3356	11·99	3253	7·85	3227	6·64
3300	13·25	3420	17·36	3331	14·67	3291	9·35
3360	18·20	3469	20·00	3406	19·47	3360	16·56
3403	19·87	3514	17·73	3429	20·02	3412	20·00
3435	20·00	3579	10·98	3443	19·10	3455	18·32
3503	14·62	3620	7·28	3492	16·30	3496	14·19
3568	7·87	3686	4·61	3543	11·56	3554	7·29
3627	5·28	3744	1·18	3619	3·92	3626	2·90
3689	0·53	...	...	3698	0·82	3670	1·42
3731	0·23	...	...	...	...	3717	0·55

The following results are noticeable from an examination of the above intensity curves:—

(*i*) Although the curves for the two solutions are equally broad, they are relatively shifted with respect to one another, the curve for $LiNO_3$ being shifted as a whole to the side of higher frequency as compared with the curves for lithium chloride and pure water.

(*ii*) As compared with the curve for pure water, the lower frequency portions of the two intensity curves for the salt solutions are concave in their shape, while the higher frequency branch of the curve for lithium nitrate is slightly convex in shape, the corresponding portion of the curve for lithium chloride being concave.

(*iii*) Although the positions of the maxima of the band in pure water and in lithium chloride solution are more or less in the same position, the lower frequency branch of the intensity curve for the latter is shifted to higher frequency as compared with that for the former and is decidedly concave in its form.

(*iv*) The bands for the solutions are sharper than that in the pure solvent—a general result noticed in the previous investigations.

The above results are largely similar to those observed with hydrochloric and nitric acids at the same concentration studied in Part I.

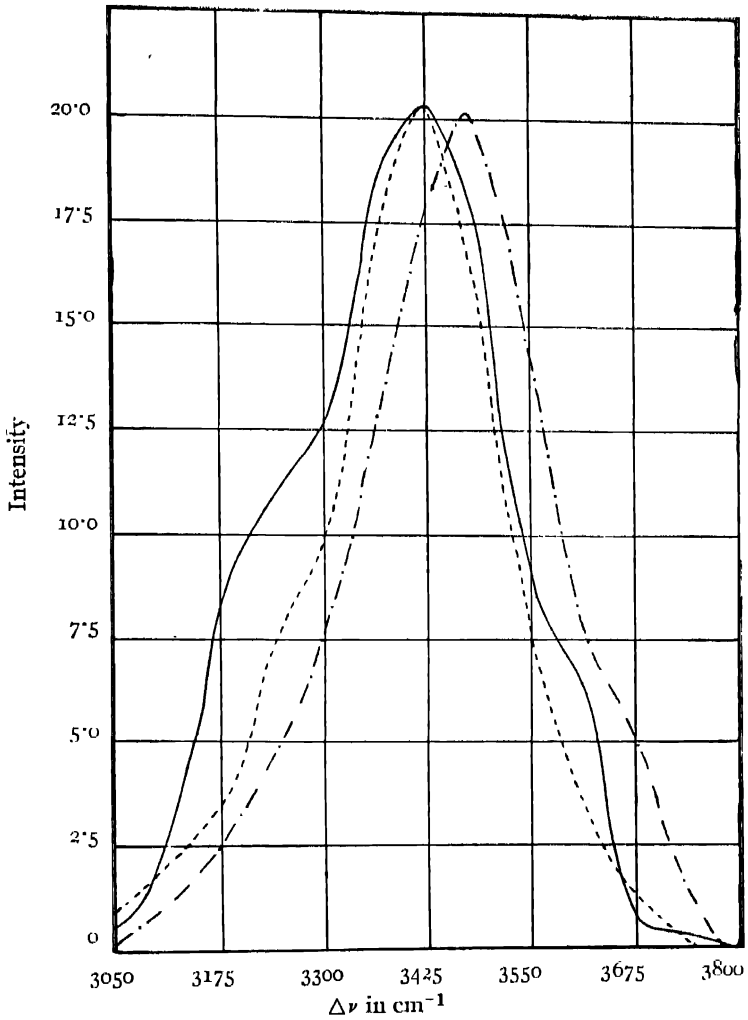

FIGURE 2

Intensity curves for the Raman water-band in solution of Li NO_3 and LiCl with the same water content.

H_2O - - ——— ; $LiNO_3$, 8N- · · · · · · · · ; LiCl, 4·2N———

In figure 2 are given the intensity curves of the Raman water-band in solutions of lithium chloride and lithium nitrate having the same water content in any definite volume, together with the curve for pure water. The concentrations of $LiNO_3$ and LiCl are respectively 8N and 4·2N. The distribution of intensity along the bands is given in table I above. As compared with the curves in figure 1 at the same concentration of the solutions, the relative shift between the curves is less in this case, although still considerable, and, further, the lower

frequency branch of the curve for lithium chloride solution has developed a slight convexity at the smaller concentration. The same result is quite obvious from figure 3, in which the intensity curves for lithium chloride at the two different concentrations are reproduced together with the curve for pure water. One more interesting result that is observed from this figure is that the band at the lower concentration is slightly *narrower* than the one at the higher—an anomalous result observed before (Part I) in the case of hydrochloric acid.

In figure 4 are given the intensity curves for the four acids, hydrochloric, sulphuric, nitric and perchloric,—all at the same concentration, 8N. The values for the distribution of intensity along the band in the first three cases are taken from Part I and for the last is contained in table II.

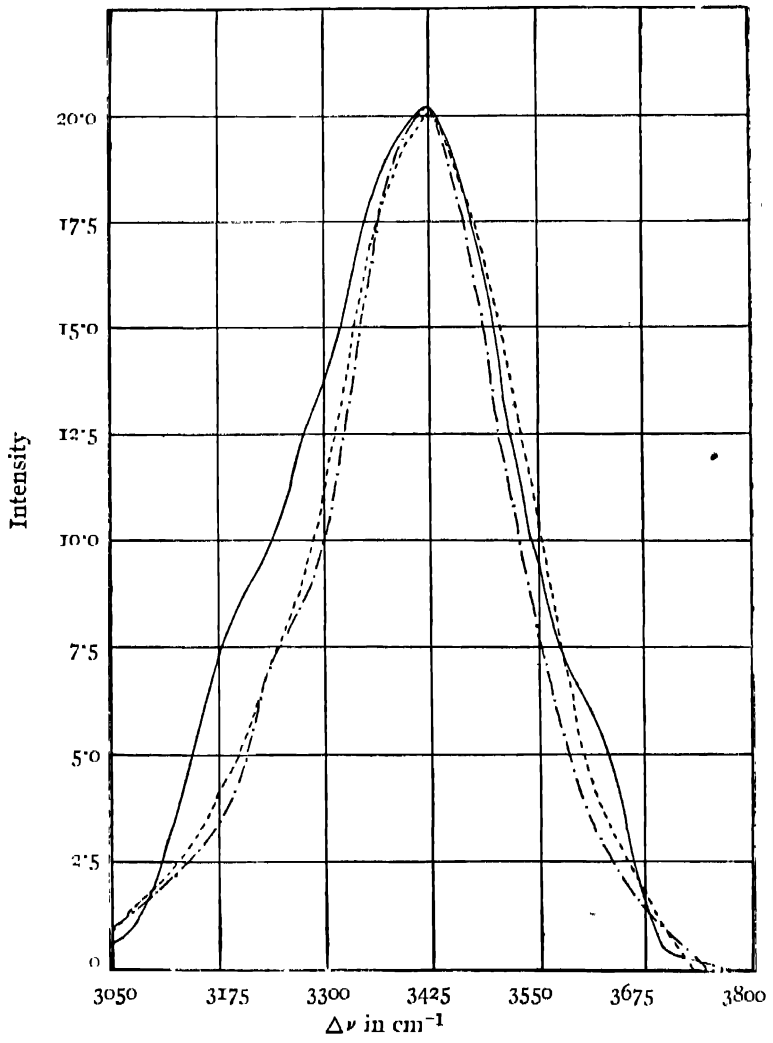

FIGURE 3

Intensity curves for the Raman water-band in solutions of LiCl at two different concentrations.

H_2O——; Li Cl, 4·2 N- · · · · · · · ·; Li Cl, 8N——

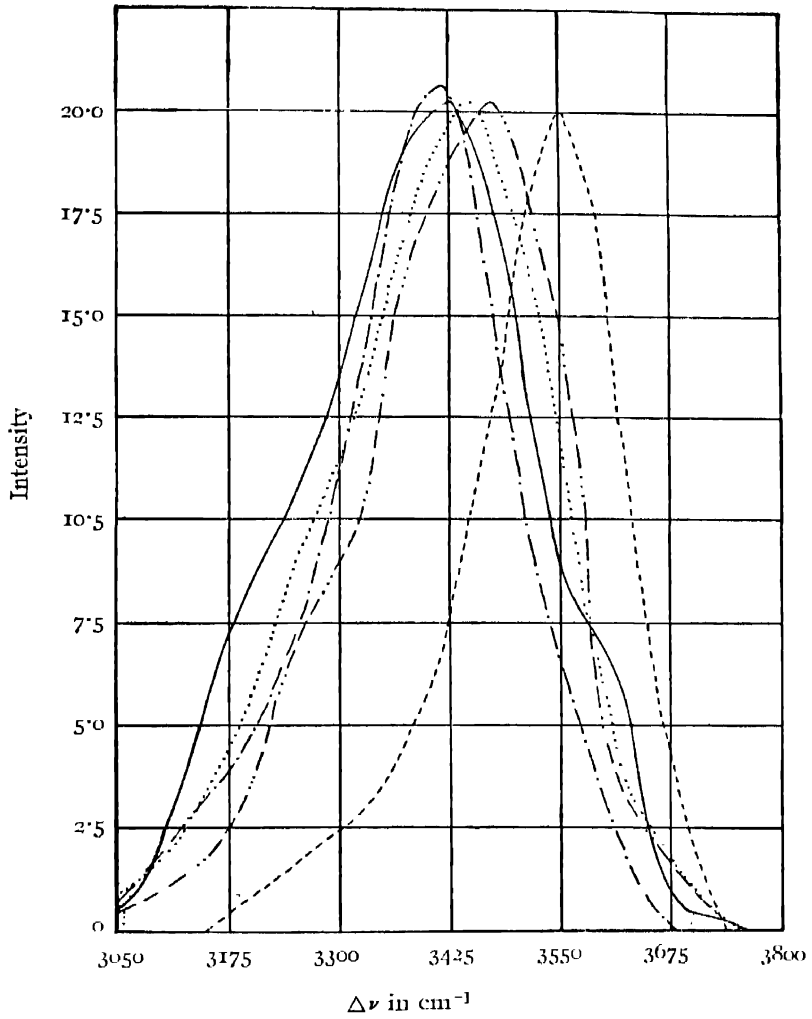

FIGURE 4

Intensity curves for the Raman water-band in solutions of *acids* at the same concentration (8N).

H_2O———; $HClO_4$, 8N- - - - - - - - HCl, 8N- · - · - · - · - ·;

HNO_3, 8N- - - ... - - -; H_2SO_4, 8N.....

TABLE II.

Intensity distribution along the water-band in

1. $HClO_4$, 8N.		2. $NaClO_4$, 6·3N		3. $NaClO_3$, 7·1N		4. $NaNO_3$ 8N	
$\delta\nu$ in cm $^{-1}$.	Intensity.	$\delta\nu$ in cm $^{-1}$	Intensity	$\delta\nu$ in cm $^{-1}$.	Intensity	$\delta\nu$ in cm $^{-1}$.	Intensity
3182	0·54	3203	2·42	3139	0·38	3122	0·28
3252	1·69	3240	4·01	3211	1·30	3204	1·45
3326	2·86	3272	5·67	3274	2·46	3297	4·02
3405	6·13	3314	7·84	3324	3·89	3380	12·01
3471	12·45	3351	10·10	3382	7·37	3458	19·78
3517	17·92	3410	13·62	3448	13·83	3492	20·00
3551	20·00	3480	18·88	3488	18·57	3526	18·46
3598	16·19	3573	20·00	3523	20·00	3571	9·54
3639	8·66	3611	15·36	3564	17·94	3614	2·59
3697	2·33	3648	8·53	3622	9·33	3728	0·74
...	...	3696	3·24	3692	2·18	...	..
...	...	3730	1·68	3758	0·26	..	..

In addition to the results noticed in the case of the first three acids as mentioned in Part I, one remarkable result observed in the case of perchloric acid here is that the water-band for the latter is extremely sharp—in fact the sharpest for all the strong electrolytes so far studied—and is shifted to a very considerable degree to the side of higher frequency, the shift being greater than in the case of any other substance studied.

Figure 5 gives the intensity curves of the water-band solutions of sodium nitrite, lithium nitrate, calcium chloride and bromide, all of them having been studied at the same concentration, *viz.*, 8N. The curve for pure water also is reproduced for purposes of comparison. The distribution of intensity along the band in the several cases is contained in tables I and III.

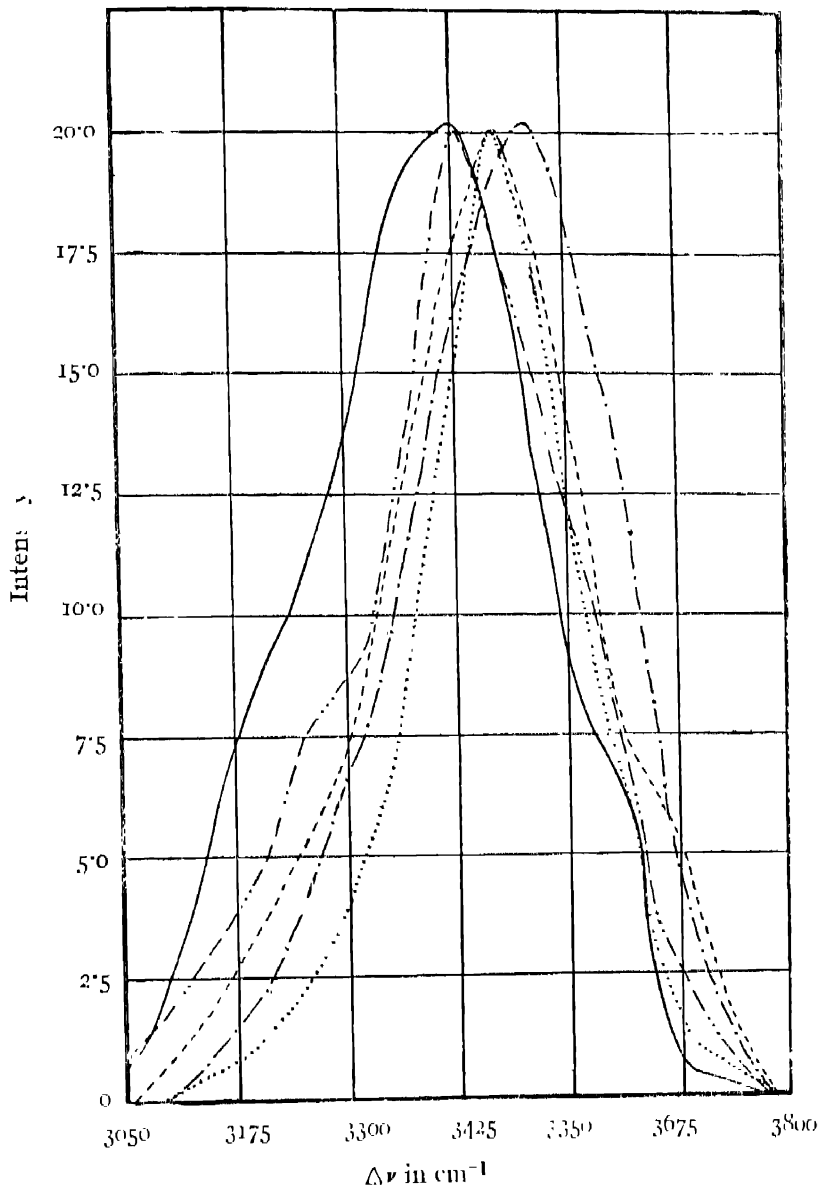

FIGURE 5

Intensity curves for the Raman water-band in solutions of *salts* at the same concentration (8N).

H_2O——; $NaNO_2$, 8N- · - · - · -; $LiNO_3$, 8N———,
$CaBr_2$, 8N.....; $CaCl_2$—— - · · · ———;

TABLE III.

Intensity distribution along the Raman water-band in

1. $NaNO_2$, 8N ,		2. $CaCl_2$, 8N ,		3. $CaBr_2$, 8N.	
$\delta\nu$ in cm $^{-1}$.	Intensity.	$\delta\nu$ in cm^{-1}.	Intensity.	$\delta\nu$ in cm^{-1}.	Intensity.
3134	0·60	3069	1·20	3115	0·22
3202	2·10	3137	2·85	3186	0·98
3274	5·36	3201	4·65	3248	2·25
3333	8·33	3251	7·36	3293	3·64
3402	14·49	3315	9·00	3359	7·41
3471	19·04	3370	13·80	3435	16·19
3517	20·00	3407	18·09	3472	20·00
3551	18·30	3430	20·00	3523	16·29
3591	14·80	3485	16·98	3585	8·42
3625	11·61	3531	13·46	3642	3·24
3664	5·86	3587	9·68	3693	1·02
3720	1.70	3646	3·82	3742	0·42
3760	0·40	3711	1·42	..	...

The curves for the other salts studied in the present investigation (*viz.*, sodium chlorate and perchlorate) are not given in this figure, as the highest concentration at which they are available is less than 8N. From an examination of the intensity curves in figure 5, the following results are obtained :—

(*i*) As compared with the band for pure water, there is a progressive shift in the position as well as the maximum of the band towards higher frequency as we pass from calcium chloride to calcium bromide and lithium nitrate to sodium nitrite, the shift in the case of the latter being the greatest.

(*ii*) There is a pronounced convexity in shape in the lower frequency branch of the intensity curve for calcium chloride and in the higher frequency branch for lithium nitrate.

(*iii*) The band for calcium bromide appears to be the sharpest.

Figure 6 contains the intensity curves of the water-band in solutions of sodium nitrate, chlorate, and perchlorate with the same water content in any given volume, their respective concentrations being 8N, 7·1N and 6·3N. The intensity distribution along the band in the three solutions and pure water is given in tables I and II. It is seen from the figure that the bands are shifted

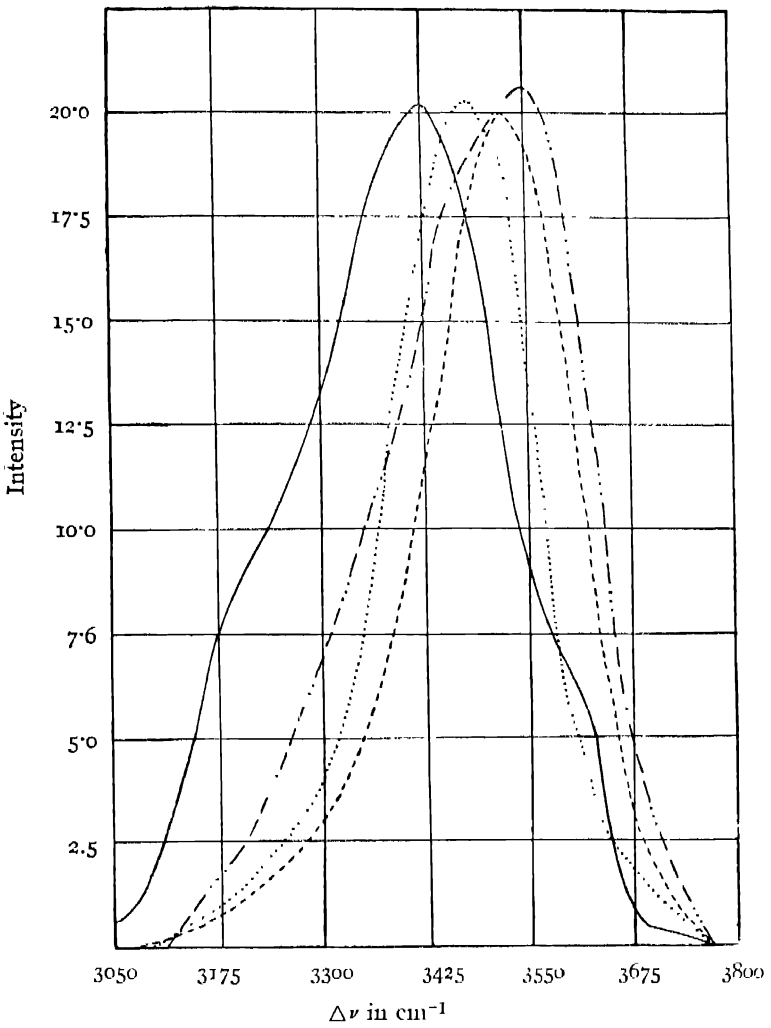

FIGURE 6

Intensity curves for the Raman water-bands in solutions of salts with the same water content.

H_2O——; $NaClO_4$, 6·3N— — —..— — —

$NaClO_3$, 7·1N - - - - - - ; $NaNO_3$, 8N.....

towards higher frequency as compared with that for pure water and relative to each other, the shift increasing from nitrate to chlorate and from chlorate to perchlorate. Further, the water-band for sodium nitrate is the sharpest and that for the perchlorate broader than the rest.

In figure 7 are given the intensity curves of the water-band in pure water and in solutions of hydrochloric acid, lithium chloride, calcium chloride and

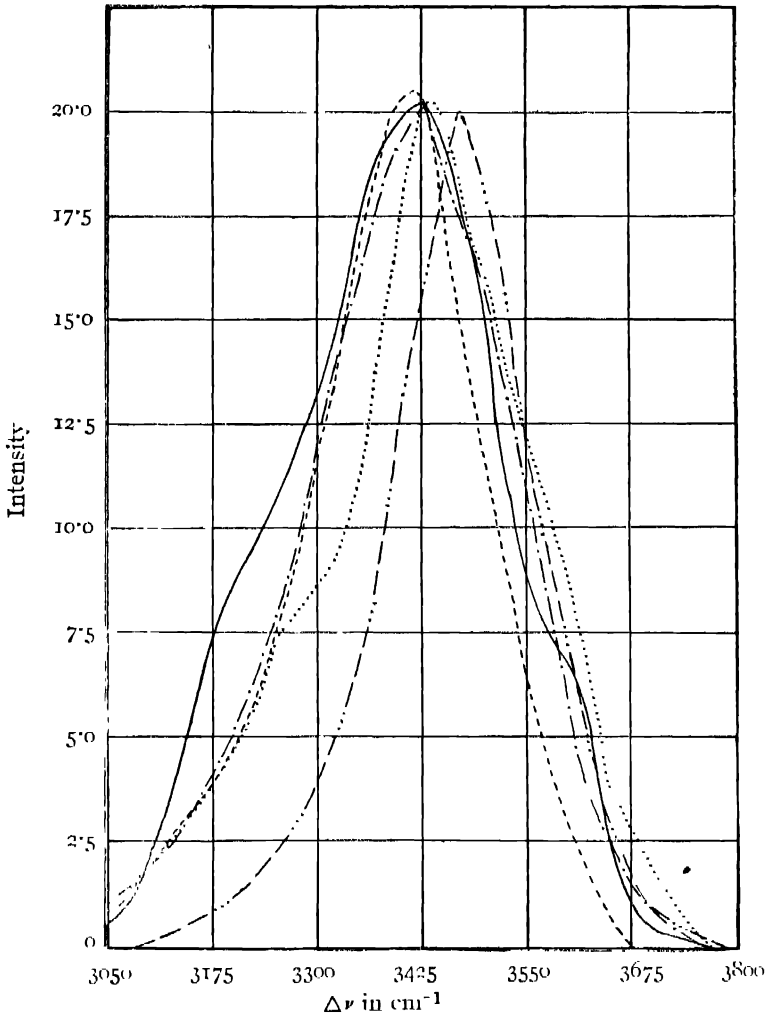

FIGURE 7

Intensity curves for the Raman water-bands in solutions of *halides* at the same concentration (8N).

H_2O——; HCl, 8N - - - - - - ; LiCl, 8N - · - · - · - ·
$CaCl_2$, 8N.....; $CaBr_2$, 8N- - - · - · - · -

bromide at the same concentration, *viz.*, 8N. This study is undertaken with a view to see whether there is any close similarity in the behaviour of all the halides as a class—a point raised in Part I of these investigations from the anomalous behaviour of hydrochloric acid, and to study the respective influence of the positive and negative ions on the constitution of the solvent. It is at once seen from the figure that the curves for all the solutions containing the chloride ion are more or less very similar, their maxima of intensity occurring nearly in the same position for all. There are, however, certain minor differences

in the sharpness of the curves. The solution of calcium bromide, on the other hand, behaves differently from the rest in that its water-band is far sharper and is shifted considerably towards higher frequency as compared with the others, thus exhibiting a clear difference again in behaviour among the halides themselves. Of the chlorides, the curve for calcium chloride solution shows a decisive convexity in shape in its lower frequency branch, while the others are concave.

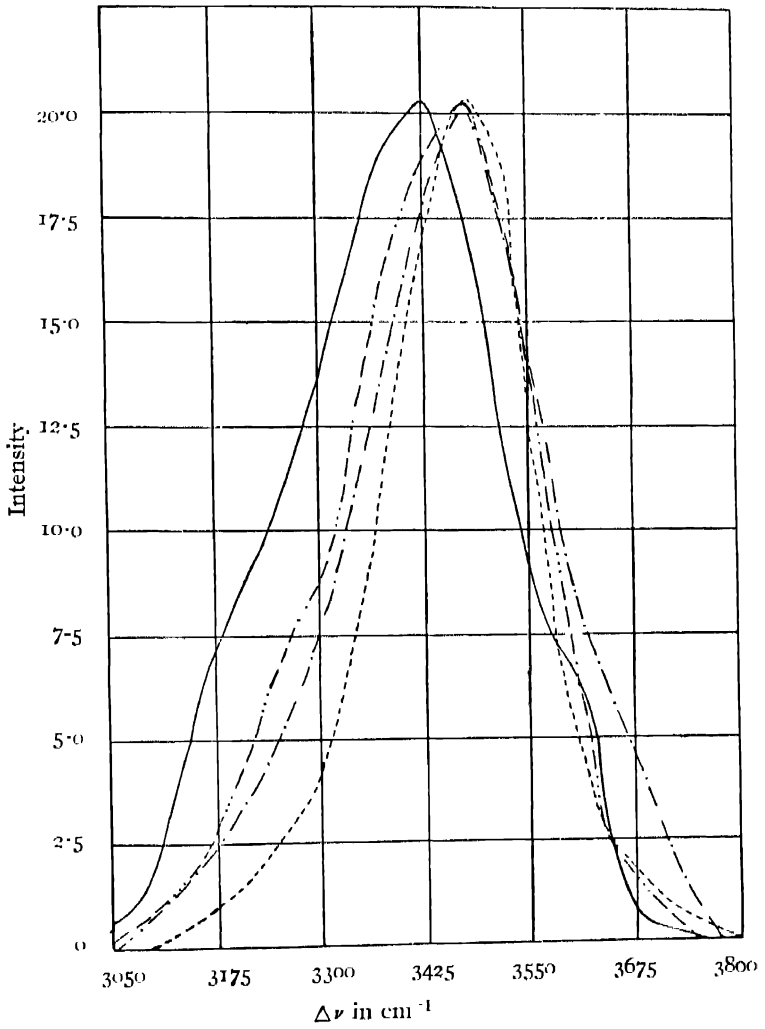

FIGURE 8

Intensity curves for the Raman water-band in solutions containing the same anion (NO_3^-) but different cations.

H_2O——; $NaNO_3$, 8N - - - - - - ; Li NO_3,8N - · - · -

HNO_3, 8N - - - - - - - - -

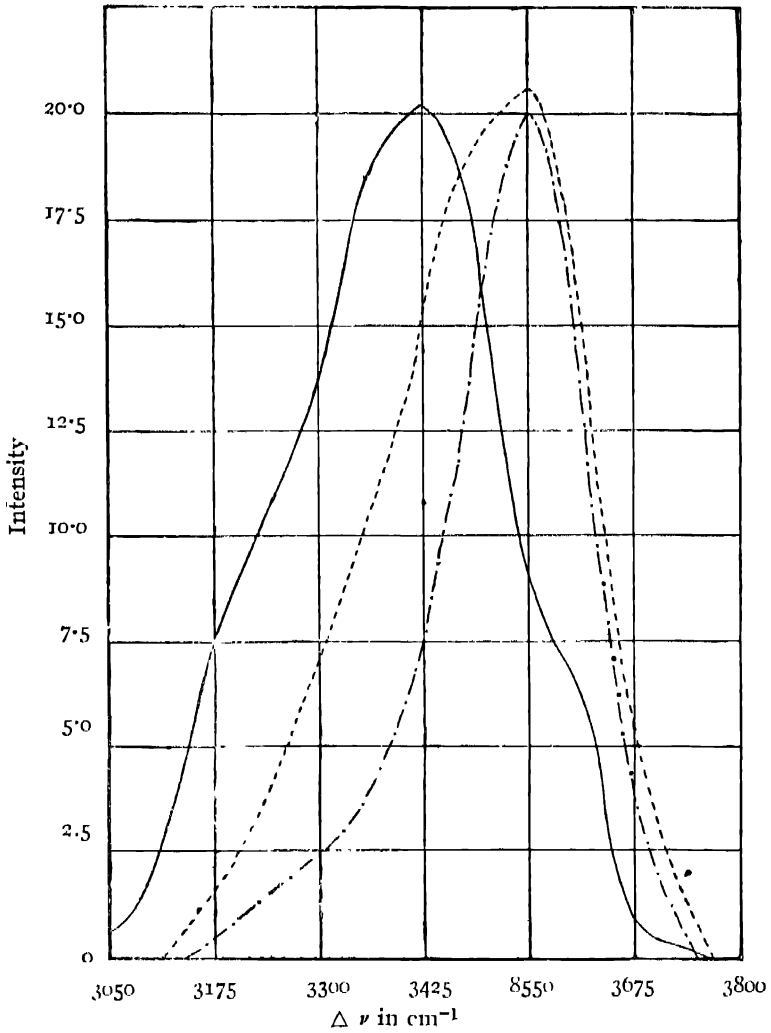

FIGURE 9

Intensity curves of the Raman water-band in solution containing the same anion (ClO_4^-), but different cations.

H_2O——; $HClO_4$, 8N - - - - - - - - - - ; $NaClO_4$, 6·3N - - - - -

Finally, in figures 8 and 9 are given the intensity curves of the water-band in solutions containing the nitrate ion (HNO_3, $NaNO_3$ and $LiNO_3$) and those containing the perchlorate ion ($HClO_4$ and $NaClO_4$) with a view to obtain greater evidence as to the behaviour of the anion and the cation.

It is seen that, except for minor differences in the sharpness of the bands, they are similar, their maxima of intensity occurring in about the same position in each figure. This indicates that the behaviour of the water-band in these solutions is characteristic of the nature of the anion and is almost independent of the cation.

Table IV contains the positions of the intensity maximum of the water-band in the several solutions studied above.

TABLE IV

Solution.	Concentration	Position of intensity maximum of water-band.
Water	...	3424 cm $^{-1}$
$LiNO_3$	8N	3474 ,,
$NaNO_3$	8N	3480 ,,
HNO_3	8N	3474 ,,
HCl	8N	3435 ,,
LiCl	8N	3435 ,,
$CaCl_2$	8N	3430 ,,
$CaBr_2$	8N	3470 ,,
LiCl	4·2N	3422 ,,
$HClO_4$	8N	3550 ,,
$NaClO_4$	0·3N	3550 ,,
$NaClO_3$	7·1N	3523 ,,
$NaNO_2$	8N	3506 ,,
H_2SO_4	8N	3440 ,,

SUMMARY OF RESULTS.

The main results noticed above may be briefly summarized as follows:—

(1) The Raman water-band in solutions of electorytes is invariably sharper than that in pure water—a general result observed in Part I.

(2) Except in the case of perchloric acid and sodium perchlorate, there is an intensification of the central component of the band corresponding to double water molecules at the expense of the other two. In the case of $HClO_4$ and $NaClO_4$, however, the third component with the higher frequency shift corresponding to single molecules appears to predominate.

(3) At the same concentration, the intensity curve for $LiNO_3$ is relatively shifted to higher frequency as compared with that for LiCl, the lower frequency branches of both the intensity curves being definitely concave in shape as compared with that for pure water which is convex. The higher frequency

branch of $LiNO_3$ is, however, slightly convex, while that for LiCl is concave.

(4) The water-band in solutions of lithium chloride is slightly narrower at the lower concentration than at the higher—an anomalous result formerly noticed in the case of hydrochloric acid.

(5) In the case of the salts at the same concentration, there is a progressive shift towards higher frequency as we pass from calcium chloride to calcium bromide and lithium nitrate to sodium nitrite, the shift in the case of the last being the greatest.

(6) Of the salts, the water-band in the case of calcium bromide appears to be the sharpest.

(7) There is a pronounced convexity in the shape of the intensity curve for calcium chloride on the side of lower frequency and towards higher frequency for lithium nitrate.

(8) The observed similarity in and blending together of the intensity curves of the water-band in solutions of the acids as described in Part I are not so obvious with the salts herein studied, considerable differences between the bands persisting even with the same water content.

(9) The behaviour of halides as a class is not similar, the chlorides behaving differently from the bromides.

(10) Of the sodium salts studied, the water-band in the case of the perchlorate appears to be the broadest.

(11) The position of the intensity maximum of the water-band is independent of the nature of the cation, but is characteristic of the anion.

4. DISCUSSION.

The results obtained in the present investigation, which is a continuation of the work published earlier in Part I, seem to be capable of a satisfactory interpretation on the same lines as before, namely, as the cumulative effect of a change in water equilibrium between the proportions of the single (H_2O), double $(H_2O)_2$ and triple $(H_2O)_3$ molecules, and of the hydration of the ions of the molecules of the dissolved substance.

Whereas the former work was primarily concerned with a study under different conditions of the influence of the three mineral acids, besides a few salts, on the constitution of water, the present one is mostly concerned with a study of some of the typical salts with regard to the same aspect of the problem. From a comparison of the results obtained in the two investigations, it is apparent that there are both points of similarity and dissimilarity between the acids and the salts with regard to their behaviour in aqueous solutions on the constitution of the solvent. The fact that the water-band in solutions is invariably sharper than that

in the pure liquid and that the central component due to the double molecules is intensified shows that there is no difference between acids and salts in this respect—all of them, in general, tending to increase the proportion of double molecules at the expense of the other two types, the extent to which they do, of course, varying for different substances of the same major group. In fact, in this particular aspect of sharpening the water-band in solutions, all substances—whether strong, weak or non-electrolytes seem to behave in a similar manner, as could be gathered from the previous work of the author [5] on the other classes of substances also.

From the similarity between the results obtained with addition of electrolytes to water and with change of temperature of the pure liquid, it was concluded in Part I before that the explanation of the former phenomena should, at least in part, be based upon the same lines as that put forward to explain the latter. And the latter was explained by Ramakrishna Rao[6] on the basis of the existence of three different types of molecules, namely $(H_2O)_1$, $(H_2O)_2$, and $(H_2O)_3$, the proportions of which vary with change of temperature. That such an explanation of the changes in the structure of the water-band in solutions on the basis of a change in water equilibrium is in a large measure true is also supported by the theoretical work of Bernal and Fowler[7] who arrived at a similar conclusion by a different line of attack of the problem from considerations of the viscosity of ionic solutions. They put forward the hypothesis of structural temperature in solutions, which they define as that temperature at which pure water would effectively have the same inner structure. They thus find that in all cases the effect of dissolved ions is to increase the structural temperature of water, which in terms of the author's interpretation means a shift in the band towards higher frequency, and this is exactly the experimental result observed in most cases. Further, the above authors find that the effect is much smaller for the chlorides with small ions, H^+, Li^+, Mg^{++}, than for those with large ions, and this result is again in perfect agreement with that of the author, who finds that the shift in the intensity maximum of the band is least in solutions of HCl and LiCl, the position of the maximum almost coinciding with that in pure water, while for the chloride with the larger ion, Ca^{++}, there is a small but clear shift, although not as much as for the other salts. The above result with the chlorides also agrees with the observations of Magat in the paper referred to before.

From a detailed study of the changes in the structure of the Raman band in pure water at different temperatures and in different states Ramakrishna Rao[8] allocated the three components of the band with intensity maxima at 3217 cm^{-1}, 3433 cm^{-1}, and 3582 cm^{-1}, to the three types of molecules $(H_2O)_3$, $(H_2O)_2$ and $(H_2O)_1$, respectively. On this hypothesis, the large intensity of the central component together with the diminution in intensity of the other two components of the band signifies that the proportion of the double or the so-called

'water' molecules is much more than that of the other two types. This interpretation is also supported by the observation of Ramakrishna Rao that dihydrol $(H_2O)_2$, is decidedly more stable in the liquid state as evidenced from its greater preponderance over the other two types in this state. Addition of electrolytes seems to contribute to enhance the instability of the latter types.

That the change in water equilibrium is not the only cause of the observed changes in the structure of the Raman water-band in electrolytic solutions and that hydration of the ions plays an important part as well has been shown in Part I. From considerations of the Raman effect of water of crytallization, that due to water of hydration has been deduced by the author in a former publication;[9] and that such an interpretation was correct is also supported by Bernal and Fowler in their paper referred to above, who arrive at the same result as to the close similarity between water of crystallization and water of hydration by a different line of theoretical reasoning based on the determination of ionic hydration as governed by Goldschmidt's co-ordination number. Now, the extent to which an ion can gather round it molecules of water of hydration depends primarily on its polarising power, that is, the ratio of its charge to its radius. Thus, large monovalent ions will have little effect, while small and highly charged ions will have the greatest. Bernal and Fowler infer from potential energy considerations that for univalent ions of radius greater than 1·6·Å, no hydration can occur, while for all mono-atomic polyvalent ions hydration will always take place. Thus, the small ions, *e.g.*, Li^+, Na^+, Mg^{++}, F^-, should be largely hydrated, while the larger ions like Rb^+, Cs^+, Cl^-, Br^-, I^-, should be least affected by water of hydration, and this is amply borne out by a lot of experimental evidence. From considerations of apparent ionic volumes and the densities of ionic solutions at great dilutions, the above authors conclude that all positive ions, except Rb^+, Cs^+, and NH_4^+, are hydrated, while all negative ions except OH^-, and F^-, are not.

This conclusion, *viz.*, that the cations are mainly responsible for the hydration effects, while the anions are for changes in the water equilibrium, is also supported from considerations of the electronic theory of valency.[10] Of the H and O atoms of the water molecule, oxygen has greater co-ordinating power and is a better donor of electrons than hydrogen is an acceptor, and the presence of a positive charge on an ion (*i.e.*, a cation) facilitates easy co-ordination between the ion and the water molecule.

Further, a few pages later, Sidgwick gives arguments from other evidences to show that, in hydrates, water molecules probably exist in pairs, thus further supporting the conclusion from Raman spectra that the enhancement of the central component of the band is due to increase in the number of double molecules in almost all solutions.

From experiments based on the transport of ions in aqueous solutions [11] the following figures were found for the relative hydrations of ions on the assumption that the number of molecules of water of hydration for H^+ is 1: K^+, 5; Na^+, 8; Li^+, 14: Cl^-, 4 Applying Stokes' law to the mobilities of ions in solutions [12] the following values are found for the relative hydrations of ions at infinite dilution: H^+, 0; OH^-, 10; K^+, Cl^- Br^-, I^-, $\frac{1}{2}SO_4^{--}$ 20; NO_3, 25; Ag^+, ClO_3^-, 35; Na^+, 70; Li^+, 150. From the above data, it is clear that the H^+ ion is the least hydrated of the smaller ions and Li^+ the most. In the case of the H^+ ion, its abnormally high mobility must also be attributed, at least in part, to its low hydration.

From the foregoing considerations, it is now easy to explain the results herein obtained with regard to the changes in the structure of the water-band in aqueous electrolytic solutions. In the case of the acids studied in Part I, it was found that, at the same water content, the intensity curves of the water-band in the different solutions became very similar in shape and position, the differences noticed at the same concentration of the solutions having disappeared to a very appreciable degree. This was taken as strong evidence in favour of the view expressed that the change in water equilibrium is the main factor contributing to the observed results in these solutions. In the case of the salts, however, both in the present investigation as well as in the previous one, considerable differences persisted even when the water content in them was equalized. These phenomena are easily intelligible when one considers the fact that, in the case of the acids, the *sparsely* hydrated H^+ ion is common to all of them, while the negative ion is generally hydrated to a negligible degree or not at all. Thus, the deciding factor in this case is the change in water equilibrium, and when the water content is equalized it is but natural that the water-band in the several acid solutions should be largely similar. In the case of the salts, however, the anions as well as the cations are different and almost all the positive ions studied (Li^+, Na^+, Ca^{++}) are largely hydrated to different degrees, the hydration in the case of Li^+ being highest. Thus in these cases, in addition to change in water equilibrium, hydration of the ions plays an equally important role, and, as it is widely different for the different ions, it is no wonder that considerable differences in the structure of the water-band persist even when the water content is equalized.

The result, that the intensity curves for lithium chloride and nitrate at the same concentration (Fig. 1) are equally broad is thus due to the large hydrating power of the common cation, Li^+, while the relative shift to higher frequency of the curve for lithium nitrate, together with the slight but definite convexity in the shape of the higher frequency branch of the intensity curve connotes that the proportion of triple molecules is considerably less and that of the single greater than in the chloride solution at the same concentration. As compared with pure

water, however, the proportion of the triple molecules is far less in both the solutions, as can be deduced from the decidedly concave shape and shift towards increasing frequency of the lower frequency branch of their intensity curves. The development of a slight convexity in the shape of the lower frequency branch of the intensity curve for lithium chloride at the lower concentration (4·2N) as compared with that at the higher signifies that at the greater dilution there is an increase in the proportion of the triple molecules together with the formation of the more complex hydrates, the component of the band corresponding to which is formed in the region of lower frequency.[13]

The extreme sharpness of the band for perchloric acid as compared with the other acids and its very large shift towards higher frequency indicates that the proportion of single molecules in this case is far larger than in the case of any other substance so far studied—in fact, they seem to be greater than the proportion of even double molecules, the proportion of the more complex triple type being negligible. Further, the remarkable sharpness of the band in this case is to be attributed to the almost negligible amount of hydration in this case as compared with the other acids and sodium perchlorate, the last of which, although containing the same anion (ClO_4^-), gives rise to a *broader* band with the same position of the intensity maximum on account of the greater hydrating power of the Na^+ ion.

In the case of the salt solutions studied at the same concentration (Fig. 5), the progressive shift to higher frequency as we pass from calcium chloride to bromide and lithium nitrate to sodium nitrite indicates a decreasing proportion of the more complex types of water molecules and hydrates in the above order, while the proportion of the triple molecules is less in all of them than in pure water, as can be seen from the diminished intensity and shift to increasing frequency of the lower frequency branch of their intensity curves. The development of a certain amount of convexity in the lower frequency portion of the intensity curve for calcium chloride perhaps denotes the presence to a larger degree of the more complex hydrates with three and more molecules of water of hydration.

The fact that the water-band in the solution of sodium perchlorate is broader than that in any of the other sodium salts studied indicates that the proportion of hydrates formed in this case is greater—an inference also supported by the well known fact that it crystallizes with water of crystallisation whereas the others do not.

Figures 7, 8, and 9 show clearly the influence of the anion and the cation on the structure of the water-band. In each figure, the maximum of intensity of the water-band falls in the same position, within the limits of experimental error, for all the solutions studied under each head, while the sharpness of the bands themselves is different for each of the solutions. From what has been discussed in the foregoing pages, the obvious explanation of these results is the following :

The position of the intensity maximum is characteristic of the negative ion or the so called anion and is independent of the nature of the cation. From the facts known from other evidences that the negative ions are, with the exception of OH^- and F^-, generally hydrated to a negligible degree, and from the above results from Raman spectra, it appears that change in water equilibrium is primarily a function of the anion. On the other hand, the widely divergent sharpness of the intensity curves in each of the above figures for solutions with the same anion, but different cations, suggests that those differences arise out of the different hydrating powers of the several cations, which are generally hydrated to a more or less appreciable degree. Thus, while changes due to water equilibrium are to be attributed to the negative ions (anions), changes in the structure of the water-band due to water of hydration are to be ascribed in the main to positive ions (cations).

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